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(54) Title: PREFORMS FOR MOULDING PROCESS AND RESINS THEREFOR (57) Abstract <p>Binder coated fibres comprising from 80 to 99 % by weight reinforcing fibres and from 1 to 20 % by weight of a preform binder resin, said binder resin being in the form of particles or discrete areas on the surface of the reinforcing fibres, said binder resin comprising: from 40 to 90 % by weight of the binder resin of a thermosetting resin and from 10 to 60 % by weight of the binder resin of a high molecular weight engineering thermoplastic and/or an elastomer selected from vinyl addition polymer, fluororelastomers and polysiloxane elastomers, the engineering thermoplastic/elastomer being dissolved in the thermosetting resin, the binder resin being non-tacky at ambient temperature, having a softening point in the range 50 to 150 °C and being heat curable at a temperature in the range 50 to 200 °C.</p>		

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PREFORMS FOR MOULDING PROCESS
AND RESINS THEREFOR

5 The present invention relates to preforms for
moulding processes, especially resin transfer moulding
(RTM) processes and to binders for use therein.

10 Various moulding processes, such as RTM processes
involve loading dry fibrous reinforcement layers into a
mould, closing the mould, introducing a thermosetting
resin composition into the mould and curing the resin
typically via the application of heat. One of the
process constraints in such a process is loading the
fibrous reinforcement into the mould. The individual
layers of fabrics must be cut and shaped to conform to
15 the various curvatures in the mould. This can be very
time consuming and difficult to do, especially for layups
involving foam cores or other core materials. It would
be desirable to assemble the fibrous reinforcement
outside of the mould and load only that structure (or
20 preform) into the mould at one time.

Preforms used for composite preparation are
typically composed of multiple layers of fibrous
material. These are assembled in a stack and shaped
prior to placing onto a mould surface for impregnation
25 with matrix resin. Known methods for preparing the dry
preform layers for moulding involve stacking multiple
layers of the woven or stitched fabric material with the
desired fibre orientation, and then stitching or stapling
the layers of material together. This is to maintain
30 uniform fibre alignment and stabilise the fabric to
prevent fraying.

The stack of material is then cut, outside of the
stitching or stapling, to the desired preformed shape.
The preform is then placed in a mould and resin injected
35 to impregnate the fabric. These methods for preform
stabilisation however, are limited to two-dimensional
(flat) structures and the stack of material cannot be
shaped to conform to a complex parts contour without

disturbing the stitching or stapling and/or causing fibre misalignment. If attempts are made to bend the preform, for example, to form a curved surface, the layers may separate or tear at the stitching.

5 The production of complex, three dimensional preforms may involve three dimensional weaving and braiding. These methods are quite labour intensive, increasing the cost for producing a complex shaped part.

10 Another method for stabilising a preform involves spraying an adhesive e.g. a hot melt adhesive, onto the surface of the layers to hold them together. Usually, the dry fabric is coated in discrete areas with a thin layer of the liquified thermoplastic polymer or
15 alternatively, a fibrous polymer is placed between the layers and heat applied to melt the polymer to provide adhesive characteristics. Such preforms are then contoured in a preforming mould to conform to the required complex shape by melting and resolidification of the polymer. This is achieved by the selective
20 application and removal of an external heat source, e.g. a hot air gun. This is a highly labour intensive operation.

 Since the hot melt adhesive is a thermoplastic polymer, it has several disadvantages. First, the binder
25 may not sufficiently wet the fibres to hold the adjacent layers together to maintain a shape after forming. Thus, if the preform is handled, such as during loading into the mould, it is possible that the fibre layers will shift. Also, such a thermoplastic material may detract
30 from the cured mechanical performance of the thermosetting matrix resin systems typically used to produce components via a resin transfer moulding process. During injection, the thermoplastic binder forms localised pockets within the component which inhibit or
35 prevent thermoset resin infiltration, reducing component strength. Thus, to form complex composite articles utilising hot melt binder requires sacrificing part

strength and Tg.

US-A-4992228 discloses a method for preparing preforms which comprises (1) applying substantially evenly onto the surface of each of one or more plies of an unimpregnated substrate material one or more non-sintering thermoplastic-like resinous compounds which are substantially free of any compound which would serve as a crosslinker for said thermoplastic, said resinous compound being in the form of a powder having a particle size less than about 500 microns and having a melting point as determined by Differential Scanning Calorimetry from about 50°C to about 70°C, in an amount of from about 3 to about 5 percent by weight based upon the weight of said substrate material; (2) fusing said powdered thermoplastic-like resinous compound on the surface of said substrate material; (3) cooling said resinous material; (4) assembling one or more plies of the thus treated substrate material and conforming said plies of said treated substrate material into a desired shape; (5) subjecting the thus shaped plies of treated substrate material at a temperature sufficient to melt said resinous compound; and (6) cooling said shaped treated plies of substrate material to a temperature below the melting point of said resinous compound; thereby forming a preshaped preform for use in moulding processes as reinforcing material.

US-A-5080857 discloses a method of moulding using a stabilised preform comprising the steps of:

- (a) providing a plurality of oriented fibre layers,
- (b) stacking the layers,
- (c) applying a solid uncatalysed thermosetting resin between each layer,
- (d) placing the stacked layers over a mould surface having a desired preform shape,
- (e) forming the layers over the mould surface,
- (f) heating the layers to melt the resin and lightly fuse the layers together,

(g) cooling to rigidify the layers to form a preform, and

(h) impregnating the preform with a thermosetting resin matrix containing a catalyst at a temperature at which the solid uncatalysed thermosetting resin will melt and mix with the resin matrix to catalyse the melted uncatalysed thermosetting resin therewith.

US-A-5427725 discloses a process to make a matrix composite comprising the steps of:

(1) contacting a reinforcing substrate with a tackifier, which contains either: (a) a single resin that is capable of at least partially curing with itself; or (b) a mixture containing resin and hardener that is capable of at least partially curing, at a temperature and for a time sufficient to partially cure the tackifier so that it adheres to the substrate but remains thermoplastic-like, and capable of further reaction, whereby a preform is made;

(2) placing one or more layers of the preform in a mould;

(3) injecting a second curable resin or resin composition that is capable of reacting with the tackifier, into the mould to impregnate the preform; and

(4) curing the tackifier and matrix resin, whereby a composite is formed.

The processes of US-A-5080857 and 5427725 are an improvement in terms of compatibility with the moulding resin.

GB 2007676, GB 2182074, EP 0309221, EP 0297674, WO89/04335, US 5,532,296 and US 4,377,657 disclose resin compositions which are suitable for use in various moulding processes. However, none of these resins are disclosed as being useful for resin transfer moulding and most are liquids or tacky at room temperature prior to curing.

US 4,757,120 discloses polyimide polymers which are reaction products of active methylene compounds and N,N'-

bismaleimide derivatives are improved by incorporating them with 2 to 15% by weight of a polyethersulfone polymer. The polymer blend is useful in producing films, mouldings, prepegs, laminates and filled composites which are particularly useful in structural components which have stability at high temperatures.

The present invention provides an improved preform binder resin for preform manufacture.

According to one aspect of the present invention there is provided binder coated fibres comprising from 80 to 99% by weight reinforcing fibres and from 1 to 20% by weight of a preform binder resin, said binder resin being in the form of particles or discrete areas on the surface of the reinforcing fibres, said binder resin comprising:

from 40 to 90% by weight of the binder resin of a thermosetting resin and

from 10 to 60% by weight of the binder resin of a high molecular weight engineering thermoplastic and/or an elastomer selected from vinyl addition polymer, fluoroelastomers and polysiloxane elastomers,

the engineering thermoplastic/elastomer being dissolved in the thermosetting resin, the binder resin being non-tacky at ambient temperature, having a softening point in the range 50 to 150°C and being heat curable at a temperature in the range 50 to 200°C.

The invention utilises a preform binder resin which comprises a thermosetting resin having an engineering thermoplastic and/or elastomer dissolved therein. The preform binder resin is a non-tacky solid at ambient temperature. The resin may be in the form of a non-agglomerating, free-flowing powder, generally having a particle size below 1500µm and typically having an average particle size in the range 100 to 500µm. The particulate binder may be applied to reinforcing fibres and heated to soften the particles causing the powder to adhere to the fibres. Alternatively, the binder resin may be applied to the reinforcing fibres from solution by

spraying, printing etc., such that upon evaporation of the solvent particles, discrete areas or islands of binder resin are formed. A continuous coating of binder resin is not desired since it deleteriously affects the drapability of the fibres. The binder coating of the invention may be in the form of a woven or non woven fabric which has fibres and good drapability and may readily be stacked and shaped and bonded by application of heat to a temperature in the range 60 to 120°C to make a preform.

The thermosetting resin is selected to be the same as or fully compatible with the matrix resin to be used in the RTM process. The presence of the dissolved thermoplastic/elastomer provides the solid characteristics and softening point properties to the binder resin and also imparts desirable properties to the finished moulded articles, in particular the toughness of the article is improved. It is known that the presence of a high molecular weight thermoplastic resin may improve the toughness of matrix resins used in RTM. However, it is not readily possible to incorporate the thermoplastic resin in the matrix resin since the presence of dissolved thermoplastic resin increases the viscosity of the matrix resin such that it will not readily flow through the reinforcing fibres during the moulding process. The presence of undissolved particulate thermoplastic resin in the matrix resin is not practical since the particulate resin is filtered by the reinforcing fibres during injection of the matrix resin. The binder coated fibres of the invention introduce the thermoplastic resin throughout the preform and hence throughout the moulded article. This is in a manner which readily improves the toughness of the moulded article without deleteriously effecting the drapability of the fabrics used in preparing the preform.

The thermosetting resins used in the invention may be selected from a wide range of resins useful in

moulding applications, including but not limited to bismaleimide resins (BMI), cyanate resins and epoxy resins.

Bismaleimide resins are heat-curable resins containing the maleimido group as the reactive functionality. The term bismaleimide as used herein includes mono-, bis-, tris-, tetrakis-, and higher functional maleimides and their mixtures as well, unless otherwise noted. Bismaleimide resins with an average functionality of about two are preferred. Bismaleimide resins as thusly defined are prepared by the reaction of maleic anhydride or a substituted maleic anhydride such as methylemaleic anhydride, with an aromatic or aliphatic di- or polyamine. Examples of the synthesis may be found, for example in U.S. Patent Nos. 3,018,290, 3,018,292, 3,627,780, 3,770,691, and 3,839,358. The closely related nadicimide resins, prepared analogously from a di- or polyamine but wherein the maleic anhydride is substituted by a Diels-Alder reaction product of maleic anhydride or a substituted maleic anhydride with a diene such as cyclopentadiene, are also useful. As used herein and in the claims, the term bismaleimide shall include the nadicimide resins.

Preferred di- or polyamine precursors include aliphatic and aromatic diamines. The aliphatic diamines may be straight chain, branched, or cyclic, and may contain heteroatoms. Many examples of such aliphatic diamines may be found in the above cited references. Especially preferred aliphatic diamines are hexanediamine, octanediamine, decanediamine, dodecanediamine, and trimethylhexanediamine.

The aromatic diamines may be mononuclear or polynuclear, and may contain fused ring systems as well. Preferred aromatic diamines are the phenylenediamines; the toluenediamines; the various methylenedianilines, particularly 4,4'-methylenedianiline; the naphthalenediamines; the various amino-terminated

polyarylene oligomers corresponding to or analogous to the formula $H_2N-Ar[X-Ar]_nNH_2$, wherein each Ar may individually be a mono- or poly-nuclear arylene radical, each X may individually be -O-, -S-, -CO₂-, -SO₂-, -O-CO-,
5 C₁-C₁₀ lower alkyl, C₁-C₁₀ halogenated alkyl, C₂-C₁₀ lower alkyleneoxy, aryleneoxy, polyoxyalkylene or polyoxyarylene, and wherein n is an integer of from about 1 to 10; and primary aminoalkyl terminated di- and polysiloxanes.

10 Particularly useful are bismaleimide "eutectic" resin mixtures containing several bismaleimides. Such mixtures generally have melting points which are considerably lower than the individual bismaleimides. Examples of such mixtures may be found in U.S. Patent
15 Nos. 4,413,107 and 4,377,657. Several such eutectic mixtures are commercially available.

Cyanate resins are heat-curable resins whose reactive functionality is the cyanate, or -OCN group. These resins are generally prepared by reacting a di- or
20 poly-functional phenolic compound with a cyanogen halide, generally cyanogen chloride or cyanogen bromide. The method of synthesis by now is well known to those skilled in the art, and examples may be found in U.S. Patent Nos. 3,448,079, 3,553,244 and 3,740,348. The products of this
25 reaction are the di- and polycyanate esters of the phenols.

The cyanate ester prepolymers may be prepared by the heat treatment of cyanate functional monomers either with or without a catalyst. The degree of polymerisation may
30 be followed by measurement of the viscosity. Catalysts may be used to assist the polymerisation. Such prepolymers and catalysts are known in the art.

Suitable cyanate resins are commercially available and may be prepared from mono-, di-, and polynuclear
35 phenols, including those containing fused aromatic structures. The phenols may optionally be fused aromatic structures. The phenols may optionally be substituted

with a wide variety of organic radicals including, but not limited to halogen, nitro, phenoxy, acyloxy, acyl, cyano, alkyl, aryl, alkaryl, cycloalkyl, and the like. Alkyl substituents may be halogenated, particularly
5 perchlorinated and perfluorinated. Particularly preferred alkyl substituents are methyl and trifluoromethyl.

Particularly preferred phenols are the mononuclear diphenols such as hydroquinone and resorcinol; the
10 various bisphenols, such as bisphenol A, bisphenol F, and bisphenol S; the various dihydroxynaphthalenes; and the oligomeric phenol and cresol derived novolacs. Substituted varieties of these phenols are also preferred. Other preferred phenols are the phenolated
15 dicyclopentadiene oligomers prepared by the Friedel-Crafts addition of phenol or a substituted phenol to dicyclopentadiene as taught in U.S. Patent No. 3,536,734.

Epoxy resins may also be utilised alone or as comonomers in the cyanate functional or bismaleimide
20 functional resin systems of the subject invention. Epoxy resins are thermosetting resins containing the oxirane, or epoxy group as the reactive functionality. The oxirane group may be derived from a number of diverse methods of synthesis, for example by the reaction of an
25 unsaturated compound with a peroxygen compound such as peracetic acid; or by reaction of epichlorohydrin with a compound having an active hydrogen, followed by dehydrohalogenation. Methods of synthesis are well known to those skilled in the art, and may be found, for
30 example, in the Handbook of Epoxy Resins, Lee and Neville, Eds., McGrawHill, 1967, in chapters 1 and 2 and in the references cited therein.

The epoxy resins useful in the practice of the subject invention are generally those that are
35 commercially available and substantially di- or polyfunctional resins. In general, the functionality should be from about 1.8 to about 8. Many such resins

are available commercially. Particularly useful are the epoxy resins which are derived from epichlorohydrin. Examples of such resins are the di- and polyglycidyl derivatives of the bisphenols, such as bisphenol A, bisphenol F, and bisphenol S; the dihydroxynaphthalenes, for example 1,4-, 1,6-, 1,7-, 2,5-, 2,6- and 2,7-dihydroxynaphthalenes; 9,9-bis[hydroxyphenyl]fluorene; the phenolated and cresolated monomers and oligomers of dicyclopentadiene as taught by U.S. Patent No. 3,536,734; the aminophenols, particularly 4-aminophenol; various amines such as 4,4'-, 1,4'- and 3,3'-methylenedianiline and analogues of methylenedianiline in which the methylene group is replaced with a C₁-C₄ substituted or unsubstituted lower alkyl, or -O-, -S-, -CO-, -O-CO-, -O-CO-O-, -SO₂-, or aryl group; and both amino, hydroxy, and mixed amino and hydroxy terminated polyarylene oligomers having -O-, -S-, -CO-, -O-CO-, -O-CO-O-, -SO₂-, and/ or lower alkyl groups interspersed between mono or polynuclear aryl groups as taught in U.S. Patent No. 4,175,175.

Also suitable are the epoxy resins based on the cresol and phenol novolacs. The novolacs are prepared by the condensation of phenol or cresol with formaldehyde, and typically have more than two hydroxyl groups per molecule. The glycidyl derivatives of the novolacs may be liquid, semisolid, or solid, and generally have epoxy functionalities of from 2.2 to about 8.

Hybrid resin systems may also be used. Suitable hybrid resin systems include the combination of bismaleimide and cyanate ester comonomers, epoxy and cyanate ester comonomers, and bismaleimide and epoxy comonomers, and the mixture thereof.

The binder resins of the subject invention further contain a dissolved engineering thermoplastic and/or elastomer. Such suitable thermoplastics have high strain to failure and glass transition temperatures above 150°C, preferably above 200°C. The thermoplastic mixture may be

a polyimide, polyetherimide (PEI), polyethersulfone (PES), polysulfone, polyetherketone, polyetheretherketone (PEEK), polyamide, polyamideimide, or the like. PEI is preferred. Elastomers useful in the invention include
5 flexible vinyl addition polymers including homopolymeric and copolymeric diene rubbers, derived from conjugated dienes of 4 to 8 carbons such as butadiene, isoprene, propylene, chloroprene, and the like. These include but are not limited to copolymers of such dienes with each
10 other and with one or more of such monomers as styrene, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, methyl methacrylate, and the like. Butadiene-acrylonitrile polymers and carboxylic-functional butadieneacrylonitrile polymers are most
15 preferred. Suitable fluoroelastomers are disclosed in Polym. Int., 26(2), 69-73, 1991. Suitable polysiloxane elastomers are disclosed in J Appl. Polym. Sci., 54(1), 83-90, 1994.

The thermoplastic/elastomers are present in amounts
20 from about 10 to about 60 percent by weight, preferably 20 to 40 percent by weight of the binder resin. The thermoplastic/elastomers may readily be dissolved in the thermosetting resin using a solvent, e.g. methylene chloride, and thereafter removing the solvent. The
25 resultant material may be ground to the desired particle size; alternatively, the solution may be spray dried.

The exact quantities of thermosetting resin and thermoplastic in the binder will vary with the individual constituents. Generally, thermosetting resins are liquid
30 and the presence of increasing amounts of dissolved thermoplastic/elastomer increases the viscosity until a solid is formed at ambient temperature. The concentration of thermoplastic is adjusted to provide a non-tacky solid having a softening point in the range 50
35 to 150°C, typically 60 to 120°C.

The resulting solid binder resin is non-tacky allowing it to be used in the form of a free-flowing,

non-agglomerating powder. The binder resin melts or softens sufficiently at moderate temperatures in the range 50 to 150°C. This allows the binder particles to bond to the surface of fibres when they are heated in contact with the fibres and cooled. Thereafter, the binder coated fibres may be shaped and bonded together to retain the desired shape by heating within the above temperature range and cooling. Preferred combinations of thermosetting resin and thermoplastic for the binder resin used in the invention include BMI/PEI, BMI/PES and Epoxy/PEI. The matrix resin used in the RTM process is preferably the same as the thermosetting resin of the binder.

The binder resin may contain up to 20% by weight of one or more additives selected from thermally conducting particles, electrically conducting particles, flame retardants, colourants, catalysts, curing agents and coupling agents. Suitable thermal conducting particles include metal particles, suitable electrically conductive particles include graphite. Preferred flame retardants include aluminium trihydrate, zinc borate and phosphorus flame retardants. Examples of coupling agents include aminosilanes.

The reinforcing fibres used in the present invention include glass fibres, carbon fibres, aramid fibres, ceramic fibres etc. and mixtures thereof. The resin binder may be applied to individual fibre tows which are then processed into a fabric or substrate or preferably the resin binder is applied to a fabric comprising the reinforcing fibres. The resin binder may be applied to one or both surfaces of the fabric.

The binder resin may be applied in the form of a powder, generally having a particle size in the range 100 to 500µm. Any convenient powder coating technique may be employed including spray coating, electrostatic coating, drop coating etc. After application of the resin binder powder the binder is heated to a temperature

in the range 50 to 150°C to soften the particles so that they bond to the fibre. The heat treatment should not be sufficient for the particles to completely melt and flow to form a continuous layer since this will deleteriously affect the drapability of the fabric. The resin binder powder is conveniently heated by passing the coated fabric under infrared lamps. Alternatively, the binder resin may be applied from solution by spraying, printing etc. to provide discrete areas of binder resin on the fibres.

The binder coated fibre of the invention may readily be draped and stacked and by application of heat and pressure so that a consolidated preform is produced which has long term ambient temperature integrity and good handleability.

The preform may be used to prepare a composite by introduction of a thermosetting matrix resin and curing the resins at a temperature of 50 to 200°C. The matrix resin may be introduced to the preform by any suitable technique. Generally, the preform is placed in a mould and the matrix resin introduced into the mould cavity to impregnate the preform.

The thermosetting resin of the binder resin and the matrix resin are preferably but not limited to the same type to ensure optimum compatibility thereby allowing full impregnation of the preform to produce a high performance composite. The presence of the dissolved thermoplastic/elastomer in the resin binder has been found to increase the toughness of the final cured composite compared to the identical composite prepared without the dissolved thermoplastic. Furthermore, other properties of the cured composite e.g. flexural strength, flexural modules, interlaminar shear strength are not deleteriously affected by the presence of the dissolved thermoplastic in the resin binder.

The invention will now be illustrated by the following Examples.

Example 1Preparation of a PEI-modified bismaleimide binder

2.5kg of PEI (General Electric Ultem 1000) was dissolved in 7.5kg of methylene chloride. 7.5kg of bismaleimide resin (Cytec 5250-4 RTM resin) was added to the PEI solution and stirred until homogeneous. The methylene chloride was then removed under vacuum at 80°C. When cooled to ambient, the resultant material was a hard, glassy like solid, which was subsequently ground into a fine powder of particle size 100 to 500µm. This powder is the binder for preform manufacture.

Example 2Powder coating of glass fabric

The binder powder from Example 1 was powder coated onto 7781-style glass fabric. The powder was evenly applied to one side of the fabric to give a coverage of 6% by weight. The powder coated fabric was then passed under an infrared heater which softened the powder, such that it adhered to the surface of the fabric. Other samples of fabric were coated at 1 and 3% by weight.

Example 3Manufacture of a preform

The powder coated fabric from Example 2 was used to produce a helmet shaped preform. Binder coated fabric was laid up inside a female mould. This was then consolidated into shape by means of a rubber bladder inflated with steam. The heat and pressure generated by the steam softened the binder and allowed the fabric plies to tack together. The helmet shaped preform was then cooled under pressure and a rigid, well consolidated preform resulted, which had long term ambient temperature integrity.

Example 4Toughness Evaluation

5 The interlaminar fracture toughness of a composite laminate produced from binder coated carbon fabric of the invention and a commercial bismaleimide resin, was compared with an equivalent laminate produced without binder.

10 To produce a binder coated fabric, an even coat of the binder of Example 1 was sprinkled by hand onto both surfaces of a 283 gsm 3K5H carbon fabric. The fabric was coated to give 3.5% by weight of binder on each side of the fabric and hence an overall binder content of 7% by weight. The fabric was then heated in an air circulation oven for 2 minutes at 120°C, to melt the binder onto the
15 fabric. The binder coated fabric was then removed from the oven and allowed to cool to ambient temperature.

Composite laminates were produced from both the binder coated fabric and standard fabric. Bismaleimide resin films of 96 gsm were applied to either side of the
20 two fabrics. The resultant materials were then cut into pieces measuring 16 x 12 inch (40.5 x 30.5cm). Ten plies of this material were then stacked together and consolidated under hand pressure. In the centre of this stack a FEP release film was positioned between the plies
25 at one end in order to produce a laminate suitable for the preparation of G_{Ic} test specimens according to AITM Test method 1.0005.

The preformed laminates were then cured in an autoclave moulding cycle for 6 hours at 190°C. The
30 resultant composite laminates were then postcured in an air circulated oven for 5 hours at 245°C.

G_{Ic} test specimens were prepared according to test method AITM 1.0005, with the weft fibres being aligned to the specimen in the longitudinal direction, with the weft
35 faces being nested in the crack plane. Six specimens were cut from both laminates and tested in order to acquire data.

For the specimens without binder the value of G_{Ic} obtained was 268.6 J/m².

For specimens with the binder the value of G_{Ic} obtained was 419.9 J/m².

5 The G_{Ic} are significantly higher for the specimens that included the binder and thus illustrate the increase to the toughness of the composite provided by use of the resin binder of the invention.

Example 5

10 Using samples as prepared in Example 4 the following properties of the cured laminates were evaluated:

Property	with binder	without binder
Flexural strength/MPa n sd cv	826.7 10 35.9 4.35	858 10 35.0 4.08
Flexural Modulus/GPa n sd cv	42.1 10 1.5 3.49	42.54 10 0.90 2.11
Interlaminar shear strength/MPa n sd cv	87.0 10 4.1 4.76	84.7 10 3.5 4.08
Glass transition temperature/°C sample 1 sample 2	291.6 295.4	289.5 292.3

n = number of specimens tested

35 sd = standard deviation

cv = coefficient of variation

Glass transition temperatures are tan δ values from dynamic mechanical thermal analysis (DMTA) measurements.

40 Results show that, for the properties measured, materials produced with the resin binder of the invention are not significantly different from those produced without the binder.

Example 6Preparation of a PES-Modified Bismaleimide Binder

400g of PES (Viktrex 5003P) was dissolved in a 1.3kg of methylene chloride. 600g of bismaleimide resin (Cycom 5250-4 RTM resin) was added to the PES solution and stirred until homogeneous. The methylene chloride was then removed under vacuum at 80°C. When cooled to ambient, the resultant material was a hard, glassy-like solid, which was subsequently ground into a powder of particle size <500µm. This powder was suitable for powder coating and preform manufacture by the techniques described in Examples 2 and 3.

Example 7Preparation of a Phenoxy Resin Modified Epoxy Binder

70g of a solid epoxy novalak resin (Ciba ECN 1273) was added to a 40% solids solution of phenoxy resin thermoplastic in methyl ethyl ketone, (Phenoxy Associates Paphen PKHS-40). A further 20g of methyl ethyl ketone was added and the mixture stirred until the epoxy novalak resin was fully dissolved. 5g of a catalyst (Anjinomoto Ajicure PN23) was then added and the mixture stirred until homogeneous. The methyl ethyl ketone solvent was then removed under vacuum at 80°C. When cooled to ambient temperature, the resultant material was a hard solid, which was subsequently ground to a particle size of <500µm. This powder could then be used as a binder resin.

Example 8Preparation of an Epoxy Binder Coated Fabric

The binder resin of Example 7 was powder coated onto 7781-style glass fabric at a coating weight of 5% as per Example 2.

Example 9Manufacture of an Epoxy Binder Preform

8 pieces (30 x 15cm) of the powder-coated fabric from Example 8 were cut and stacked together. This stack
5 of fabric was then consolidated under vacuum pressure using a vacuum bag. The vacuum bag was then placed in an oven at 80°C for 10 minutes to soften the binder and tack together the fabric plies. After cooling to ambient
10 temperature the vacuum bag was removed and a well consolidated preform resulted, which had long term ambient temperature integrity.

Example 10Toughness Evaluation

The binder of Example 6 was used to prepare G_{Ic}
15 specimens as per Example 4. Testing was performed according to the AITM 1.0005 test method. For specimens with binder a value for G_{Ic} of 447.9J/m² was obtained. This compares with a value for G_{Ic} of 268.6J/m² without
20 binder. This demonstrates a significant increase to the toughness of the composite provided by use of the resin binder of the invention.

Example 11Preparation of a Polysulphone Modified Epoxy Binder

25g of polysulphone (Amoco P1800) was dissolved in
25 100g of methylene chloride. 76g of a solid novalak resin (Ciba ECN 1273) was added to the solution and stirred until dissolved. 1g of a catalyst (Ciba DY9577) was then added and the mixture stirred until homogeneous. The methylene chloride was then removed under vacuum at 70°C.
30 When cooled to ambient temperature the resultant material was a hard solid, which was subsequently ground to a particle size of <500µm. This powder could then be used as a binder resin.

Example 12Preparation of an Epoxy Binder Coated Fabric

5 The binder resin of Example 11 was coated onto 3K5H carbon fabric at a coating weight of 6% following the procedure of Example 2.

Example 13Manufacture of an Epoxy Binder Preform

10 Eight pieces (33 x 18cm) of the powder coated fabric from Example 12 were cut and stacked together. The plies were consolidated at 80°C following the procedure of Example 9. A well consolidated preform with long term ambient temperature integrity resulted.

CLAIMS

1. Binder coated fibres comprising from 80 to 99% by weight reinforcing fibres and from 1 to 20% by weight of a preform binder resin, said binder resin being in the form of particles or discrete areas on the surface of the reinforcing fibres, said binder resin comprising:
 - from 40 to 90% by weight of the binder resin of a thermosetting resin and
 - from 10 to 60% by weight of the binder resin of a high molecular weight engineering thermoplastic and/or an elastomer selected from vinyl addition polymer, fluoroelastomers and polysiloxane elastomersthe engineering thermoplastic/elastomer being dissolved in the thermosetting resin, the binder resin being non-tacky at ambient temperature, having a softening point in the range 50 to 150°C and being heat curable at a temperature in the range 50 to 200°C.
2. Binder coated fibres as claimed in Claim 1 in which said binder resin comprises about 75% by weight of thermosetting resin/elastomer and about 25% by weight of engineering thermoplastic.
3. Binder coated fibres as claimed in Claim 1 or Claim 2 in which the thermosetting resin is selected from bismaleimide resins, cyanate resins and epoxy resins.
4. Binder coated fibres as claimed in Claim 3 in which the thermosetting resin is a bismaleimide resin.
5. Binder coated fibres as claimed in any preceding claim in which the engineering thermoplastic has a Tg of at least 150°C and is selected from polyimide, polyetherimide, polyethersulfone, polysulfone, polyetherketone, polyetheretherketone, polyamide, polyamideimide and phenoxy resin.
6. Binder coated fibres as claimed in Claim 5 in which the engineering thermoplastic is a polyetherimide, polyethersulfone or phenoxy resin.
7. Binder coated fibres as claimed in any preceding Claim in which the elastomer is a homopolymeric or

copolymeric diene rubber derived from a conjugated diene having from 4 to 8 carbon atoms.

8. Binder coated fibres as claimed in Claim 7 in which the elastomers is a butadiene-acrylonitrile polymer or a
5 carboxylic-functional butadiene acrylonitrile polymer.

9. Binder coated fibres as claimed in any preceding Claim in which the binder resin comprises up to 20% by weight of one or more additives selected from thermally conducting particles, electrically conducting particles,
10 flame retardants, colourants, catalysts, curing agents and coupling agents.

10. Binder coated fibres as claimed in any preceding claim in which the reinforcing fibres are selected from glass fibres, carbon fibres, aramid fibres, ceramic
15 fibres and mixtures thereof.

11. Binder coated fibres as claimed in Claim 11 in which the reinforcing fibres are in the form of a fabric.

12. Binder coated fibres as claimed in Claim 11 comprising from 90 to 97% by weight reinforcing fibres
20 and from 3 to 10% by weight of binder resin which is coated on one surface of the fabric or on both sides of the fabric.

13. Binder coated fibres as claimed in any preceding Claim in which the binder resin is in the form of
25 particles having a particle size of not more than 1500 μ m.

14. Binder coated fibres as claimed in Claim 13 in which the binder resin is in the form of particles having an average particle size in the range 100 to 500 μ m.

15. A binder resin which is a non-tacky solid at ambient
30 temperatures, has a softening point in the range 50 to 150°C and being heat curable at a temperature in the range 50 to 200°C and comprises:

from 40 to 90% by weight of a thermosetting resin
and

35 from 10 to 60% by weight of a high molecular weight engineering thermoplastic and/or an elastomer which is a rubbery vinyl addition polymer with the proviso that when

the engineering plastic is polyethersulfone it is present in an amount of from 20 to 60% by weight.

16. A binder resin as claimed in Claim 15 consisting of:

40 to 90% by weight of a thermosetting resin,

5 10 to 60% by weight of a high molecular weight engineering thermoplastic and/or an elastomer selected from vinyl addition polymer, fluoroelastomers and polysiloxane elastomers,

10 up to 20% by weight of one or more additives selected from thermally conducting particles, electrically conducting particles, flame retardants, colourants, catalysts, curing agents and coupling agents.

17. A binder resin as claimed in Claim 15 or Claim 16 in which the components are as defined in any one of Claims
15 2 to 8.

18. A binder resin as claimed in any one of Claims 15 to 17 in the form of a non-agglomerating free flowing powder having a particle size of not more than 1500 μ m.

19. A binder resin as claimed in Claim 18 having an
20 average particle size in the range 100 to 500 μ m.

20. A method of preparing a stabilised preform comprising the steps of:

providing a plurality of layers of binder coated fibres as claimed in any one of Claims 1 to 18,

25 forming the layers over a mould surface, heating the layers to a temperature in the range 50 to 150°C to melt the binder resin and fuse the layers together and cooling to rigidify the layers to form a preform.

21. A process for making a composite comprising the
30 steps of:

providing a preform produced by the method claimed in Claim 20,

35 applying a thermosetting matrix resin to the preforms and curing the resins at a temperature in the range 50 to 200°C whereby a composite is formed.

22. A process as claimed in Claim 21 in which the preform is placed in a mould.

23. A process as claimed in Claim 22 in which the matrix resin is introduced into the mould containing the preform.

- 5 24. A process of making a composite as claimed in Claim 23 in which the matrix resin is of the same type as the thermosetting resin of the binder resin.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01268

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29B11/16 B29B15/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B29B B29C C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 29 41 785 A (TECHNOCHEMIE GMBH) 30 April 1981	15-17, 20-22, 24
Y	see page 10, line 2 - page 18, line 2; claims 1-7	1-14, 18, 19, 23
X	DE 38 24 705 A (CIBA-GEIGY AG) 2 February 1989	15-17
	see page 4, line 55 - page 6, line 56; example 15	
X	US 4 962 162 A (HIROYUKI KOSUDA ET AL) 9 October 1990	15-17
	see column 6, line 14 - line 23; example 16	
Y	WO 96 37354 A (THE DOW CHEMICAL COMPANY) 28 November 1996	1-14, 18, 19, 23
	see page 5, line 21 - line 23	
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

*** Special categories of cited documents :**

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 26493 A (THE DOW CHEMICAL COMPANY) 24 November 1994 see claims 1-10; examples 1-3 ----	1-14, 18, 19, 23
A	US 5 120 823 A (JACK D. BOYD) 9 June 1992 see column 7, line 31 - line 42 ----	2-9
A	US 5 480 603 A (LEONARDO C. LOPEZ ET AL) 2 January 1996 see claims 1, 2, 12, 13, 16-20 ----	1, 20-24
A	DE 34 16 855 A (BASF AG) 14 November 1985 see claim 5 ----	1, 15
A	DATABASE WPI Week 9027 Derwent Publications Ltd., London, GB; AN 90-204895 XP002073907 & JP 02 135 229 A (IND. TECHN. RES. INST.), 24 May 1990 see abstract ----	21
A	US 5 057 353 A (ARTUN MARANCI ET AL) 15 October 1991 see examples 4, 11 see column 6, line 5 - line 37 -----	15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01268

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 2941785 A	30-04-1981	FR 2467907 A GB 2060490 A, B	30-04-1981 07-05-1981
DE 3824705 A	02-02-1989	CH 672494 A FR 2618444 A GB 2207676 A JP 1065118 A NL 8801859 A SE 8802698 A	30-11-1989 27-01-1989 08-02-1989 10-03-1989 16-02-1989 24-01-1989
US 4962162 A	09-10-1990	JP 6043508 B JP 63221122 A JP 1717298 C JP 4003770 B JP 63221139 A JP 2106902 C JP 63086758 A DE 3751984 D DE 3751984 T EP 0262891 A	08-06-1994 14-09-1988 14-12-1992 24-01-1992 14-09-1988 06-11-1996 18-04-1988 06-02-1997 17-04-1997 06-04-1988
WO 9637354 A	28-11-1996	US 5698318 A AU 5797396 A EP 0827444 A NO 975358 A PL 323488 A	16-12-1997 11-12-1996 11-03-1998 21-11-1997 30-03-1998
WO 9426493 A	24-11-1994	US 5427725 A AT 157586 T AT 157587 T AU 684782 B AU 6769394 A AU 684783 B AU 6769494 A BR 9406678 A BR 9406679 A CA 2161140 A DE 69405391 D DE 69405391 T DE 69405392 D	27-06-1995 15-09-1997 15-09-1997 08-01-1998 12-12-1994 08-01-1998 12-12-1994 23-01-1996 23-01-1996 24-11-1994 09-10-1997 12-03-1998 09-10-1997

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01268

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9426493 A		DE 69405392 T	12-03-1998
		EP 0697945 A	28-02-1996
		EP 0697946 A	28-02-1996
		ES 2108994 T	01-01-1998
		ES 2106537 T	01-11-1997
		FI 955317 A	06-11-1995
		FI 955318 A	06-11-1995
		JP 8509921 T	22-10-1996
		JP 8509922 T	22-10-1996
		NO 954435 A	06-11-1995
		NO 954436 A	06-11-1995
		WO 9426492 A	24-11-1994
		US 5721051 A	24-02-1998
		US 5427726 A	27-06-1995
US 5120823 A	09-06-1992	US 5037689 A	06-08-1991
		EP 0383174 A	22-08-1990
		JP 3197559 A	28-08-1991
		US 5189116 A	23-02-1993
US 5480603 A	02-01-1996	EP 0759842 A	05-03-1997
		JP 10500636 T	20-01-1998
		WO 9532085 A	30-11-1995
		US 5593758 A	14-01-1997
DE 3416855 A	14-11-1985	EP 0163894 A	11-12-1985
		JP 60240744 A	29-11-1985
		US 4649080 A	10-03-1987
US 5057353 A	15-10-1991	US 4957801 A	18-09-1990
		CA 2016864 A	17-11-1990
		EP 0399220 A	28-11-1990
		EP 0707032 A	17-04-1996
		JP 2311538 A	27-12-1990